# On the Reagents for the Separation and Determination of Potassium, Rubidium and Cesium

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# On the Reagents for the Separation and Determination of Potassium, Rubidium and Cesium

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During the course of an investigation of the solubility of difficultly soluble potassium, rubidium and cesium salts, it has been found that the solubility difference between two salts would change depending on the molecular weights of the salts, the number of alkali elements in the chemical formulas of the salts and the number of molecules of water of crystallization. The relationships between the solubility of potassium, rubidium and cesium salts may be expressed as follows, based on the experimental data

$$-\log {}_{n}S_{Rb}{}_{n}A = -\log {}_{n}S_{K}{}_{n}A \times \frac{n}{2}\left[(2-n)\left\{n-\left(\frac{R_{M.w.}}{500}\right)^2+\frac{R_{M.w.}}{200}\right\}\right]$$

$$-\log {}_{n}S_{Cs}{}_{n}A = -\log {}_{n}S_{Rb}{}_{n}A + \frac{n}{2}\left\{\frac{R_{M.w.}}{\left(1-\frac{R_{M.w.}}{1545}+\frac{w}{27}\right)\times 866}\right\}$$

From these equations, the conditions necessary for the quantitative separation of potassium, rubidium and cesium were clarified and it was found that $Na_2AgBi(NO_2)_6$ would best satisfy the necessary conditions as a reagent for the separation of potassium from rubidium, and $NaBiI_4$ or $KBiI_4$ as the reagent for rubidium and cesium.

## INTRODUCTION

Since potassium, rubidium and cesium are similar in their chemical behavior, it is comparatively difficult to separate and estimate each component from their mixtures exactly. Several analytical methods for these elements have already been reported, but those methods are not based on the specific or the selective reactions in separating these elements and therefore they are often apt to bring about a large error. Also, the separation of potassium, rubidium and cesium from their mixtures of various concentrations is not satisfactory even when using an ion-exchange resin. Moreover, in connection with the preparation of carrier free cesium-137 fission products and the utilization of cesium-137 as a tracer element etc., the chemical separation and determination of these elements has recently become quite important.

For these reasons, this research was done in order to find out the appropriate reagents by which potassium, rubidium and cesium could be specificially and quantitatively separated. If such a reagent is to be found, the solubility difference between two difficultly soluble salts which may be produced by the reagent should be very large. And if the solubility difference between two dif-

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ficultly soluble salts can be formulated in terms of certain variables, better reagents than the conventional reagents can be expected to be found based on such relationships. For this purpose, the solubility data of difficulty soluble salts of potassium, rubidium were listed and the relationships with regard to the solubility differences between two difficultly soluble salts were found. Moreover, on the basis of these relationships, two appropriate reagents were selected and have been experimentally shown to be satisfactory for the specific separation of potassium, rubidium and cesium. Therefore the development of the analytical method using these reagents will be seen in the various parts of the following studies.

## CONSIDERATION

During the course of an investigation of purification, separation and the determination of potassium, rubidium and cesium, the following characteristics with regard to the solubility between the difficultly soluble salts of theses elements were found : the solubility difference between two difficultly soluble salts becomes much larger with an increase of (1) the molecular weights of the salts and (2) the number of alkali elements in the chemical formulas of the salts. (3) If water of crystallization is attached to the salts, the solubility difference decreases, and (4) the solubility difference in a non-aqueous solvent is much larger than that in an aqueous medium.

Since these characteristics are still qualitative, it is desirable to represent them quantitatively in order to define the characteristics more precisely. Therefore, a quantitative formulation of the relationships of the solubilities between two difficultly soluble salts was sought, using the above-mentioned characteristics as variables.

Tôei has recently reported the quantitative relationshiqs of the solubilities between difficultly soluble potassium, rubidium and cesium salts. However, unfortunately, his relationships hold only for the limited number of organic compounds in which the number of alkali elements is always one, and do not hold for any other compounds.

Now, the following notations will be used to formulate the above characteristics.

$MnA$ : difficultly soluble salts of an alkali element.
M : Potassium, rubidium and cesium etc.
A : anion.
$n$ : the number of alkali elements.
$S_{MnA}$ : the mole number of $MnA$ dissolved in 1000 grams of solvent (water) at 20°C.
$P_{M.W.}$ = (the molecular weight of $MnA$) − (the atomic weight of alkali element) $\times n$.

Table 1. shows the compounds of which the solubility data can be used for this study and their values of $R_{M.W.}$, $-\log nS_{KnA}$, $-\log nS_{RbnA}$ and $-\log nS_{CsnA}$. Then, the following equation which indicates the relationshiqs between the solubility of a potassium salt and that of a corresponding rubidium salt, has been

Table 1.

| Compound | RM.W. | $-\log n S_K n_A$ | $-\log n S_{Rb} n_A$ | $-\log n S_{Cs} n_A$ |
|---|---|---|---|---|
| Hexyl[3] | 436 | 2.93 | 3.30 | 3.54 |
| Di-Hexyl[3] | 618 | 1.93 | 2.43 | 3.21 |
| $\alpha$-Hexyl[3] | 419 | 3.40 | 3.80 | 4.15 |
| Thio-Hexyl[3] | 394 | 3.52 | 4.15 | 4.69 |
| Tetranitro-acridon[3] | 374 | 3.38 | 3.76 | 4.03 |
| Tetranitro-phenothiazin-5-Oxyd[3] | 410 | 3.47 | 4.14 | 4.59 |
| 2,4-Dinitro-naphthsultam[3] | 270 | 2.46 | 2.70 | 2.84 |
| $M \cdot O \cdot C_6H_2(NO_2)_3$[4] | 228 | 1.72 | 1.92 | 2.07 |
| $M \cdot B(C_6H_4)_4$[5] | 319 | 3.83 | 4.35 | 4.49 |
| $M \cdot HC_4H_4O_6$[4] | 149 | 1.54 | 1.44 | 0.60 |
| $M \cdot ReO_4$[6] | 250 | 1.48 | 1.50 | 1.69 |
| $M_2PtCl_6$[7] | 408 | 1.50 | 3.01 | 3.59 |
| $M_2TeBr_6$[8] | 608 | 0.72 | 2.19 | 3.34 |
| $M_2IrCl_6$[9] | 406 | 1.28 | 2.71 | 3.48 |
| $M_2SnCl_6$[10] | 332 | 2.03 | 3.11 | — |
| $M_2 \cdot Cr_2(SO_4)_4 \cdot 24H_2O$[11] | 920 | — | 1.1 | 1.80 |
| $M_2 \cdot Fe_2(SO_4)_4 \cdot 24H_2O$[11] | 928 | — | 0.51 | 1.34 |
| $M_2 \cdot V_2(SO_4)_4 \cdot 24H_2O$[11] | 918 | — | 0.74 | 1.66 |
| $3MCl \cdot TlCl_3 \cdot 2H_2O$[12] | 453 | — | 0.25 | 0.97 |
| $M \cdot Cl$[13] | 35.5 | −0.62 | −0.78 | −0.88 |
| $M \cdot Cl$[13] | 35.5 | 2.38 | 1.76 | 0.74 |
| $M \cdot Cl$[13] | 35.5 | 3.10 | 2.65 | 1.85 |
| $M \cdot ClO_4$[14] | 99.5 | 0.92 | 1.28 | 1.16 |
| $M_2 \cdot SO_4$[15] | 96 | 0.10 | −0.16 | −0.22 |
| $M_2 \cdot SO_4$[16] | 96 | 4.12 | 3.67 | 2.44 |
| $M \cdot IO_4$[17] | 191 | 1.54 | 1.63 | 1.20 |

developed, based on the experimental fact that the solubility difference between a potassium salt and a rubidium salt are much more influenced by the values of $n$ and RM.W. than by any other factors. Therefore, in equation (1), it has been assumed that the value of $\log n S_{Rb} n_A / \log n S_K n_A$ is a function of $n$ and RM.W..

$$-\log n S_{Rb} n_A = -\log n S_K n_A \times \frac{n}{2}\left[(2-n)\left\{n-\left(\frac{\text{RM.W.}}{500}\right)^2\right\}+\frac{\text{RM.W.}}{200}\right] \quad \cdots\cdots\cdots\cdots(1)$$

The values of $-\log n S_{Rb} n_A$ calculated from equation (1) using the known values of $-\log n S_K n_A$ and the experimental values of $-\log n S_{Rb} n_A$ are shown in Table 2. It is seen from Table 2 that there is a fairly good accordance between the theoretical values and the experimental ones. Therefore, equation (1) may be considered reasonably satisfactory for representing the relationship between the soubility of a potassium salt and that of a corresponding rubidium salt. Similarly, the relationship between $-\log n S_{Cs} n_A$ and $-\log n S_{Rb} n_A$ has been found and expressed in equation (2) in which the difference between $-\log n S_{Cs} n_A$ and $-\log n S_{Rb} n_A$ has been considered as a function of $n$, RM.W. and W. Here W means the number of the water of crystallization in the difficultly soluble salt.

Table 2.

| Compound | $-\log n S_{Rb} n_A$ | | Difference |
|---|---|---|---|
| | Theoretical | Experimental | |
| $M_2 \cdot PtCl_6$ | 3.06 | 3.01 | 0.05 |
| $M_2 \cdot TeBr_6$ | 2.19 | 2.19 | 0.00 |
| $M_2 \cdot IrCl_6$ | 2.60 | 2.71 | 0.11 |
| $M_2 \cdot SnCl_6$ | 3.37 | 3.11 | 0.26 |
| $\alpha$-hexyl | 4.06 | 3.80 | 0.26 |
| Thio-hexyl | 4.13 | 4.15 | 0.02 |
| Tetranitro-acridon | 3.89 | 3.76 | 0.13 |
| Tetranitro-phenothiazin-5-Oxyd | 4.13 | 4.14 | 0.01 |
| 2,4-Dinitro-naphthsultam | 2.53 | 2.70 | 0.17 |
| $M \cdot B(C_6H_5)_4$ | 4.18 | 4.35 | 0.17 |
| $M \cdot O \cdot C_6H_2 \cdot (NO_2)_3$ | 1.66 | 1.92 | 0.26 |
| Hexyl | 3.55 | 3.30 | 0.25 |
| $M \cdot HC_4H_4O_6$ | 1.28 | 1.44 | 0.16 |
| $M \cdot ReO_4$ | 1.48 | 1.50 | 0.02 |

Table 3.

| Compound | $-\log n S_{Cs} n_A$ | | Difference |
|---|---|---|---|
| | Theoretical | Experimental | |
| $M_2 \cdot PtCl_6$ | 3.65 | 3.59 | 0.06 |
| $M_2 \cdot TeBr_6$ | 3.35 | 3.34 | 0.01 |
| $M_2 \cdot IrCl_6$ | 3.35 | 3.48 | 0.13 |
| $M_2 \cdot Cr_2(SO_4)_4 \cdot 24H_2O$ | 1.92 | 1.80 | 0.12 |
| $M_2 \cdot Fe_2(SO_4)_4 \cdot 24H_2O$ | 1.35 | 1.34 | 0.01 |
| $M_2 \cdot V_2(SO_4)_4 \cdot 24H_2O$ | 1.56 | 1.66 | 0.10 |
| Di-hexyl | 3.52 | 3.21 | 0.32 |
| $\alpha$-Hexyl | 4.13 | 4.15 | 0.02 |
| Thio-Hexyl | 4.46 | 4.69 | 0.23 |
| Tetranitro-acridon | 4.04 | 4.03 | 0.01 |
| Tetranitro-phenothiazin-5-Oxyd | 4.46 | 4.59 | 0.13 |
| 2,4-Dinitro-naphthsultam | 2.89 | 2.84 | 0.05 |
| $3M \cdot Cl \cdot TlCl_3 \cdot 2H_2O$ | 1.25 | 0.97 | 0.28 |
| $M \cdot B(C_6H_5)_4$ | 4.58 | 4.49 | 0.09 |
| $M \cdot O \cdot C_6H_2 \cdot (NO_2)_3$ | 2.08 | 2.07 | 0.01 |
| Hexyl | 3.65 | 3.54 | 0.11 |
| Hexyl | 3.60 | 3.51 | 0.09 |

$$-\log n S_{Cs} n_A = -\log n S_{Rb} n_A + \frac{n}{2}\left\{\frac{R_{M.W.}}{\left(1-\frac{R_{M.W.}}{1545}+\frac{W}{27}\right)\times 866}\right\} \quad \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

The values of $-\log n S_{Cs} n_A$ calculated by equation (2) using the known values of $-\log n S_{Rb} n_A$ and the experimental values of $-\log n S_{Cs} n_A$ are shown in Table 3. From Table 3, it is seen that these values are in fairly good agreement. There-

fore it is concluded that equation (2) satisfactorily represents the relationship between the solubility of a rubidium salt and that of a corresponding cesium salt.

In the derivation of equations (1) and (2), though the influence of a non-aqueous solvent on the solubility has been disregarded, the solubility difference between the two corresponding salts in a non-aqueous solvent is found to be larger than that in an aqueous solvent. A few examples of this are shown in Table 4. The above discussion may be summarized as follows :

Table 4, Effect of the solvent.

| solvent | | $\log n S_{Rb} n_A - \log n S_K n_A = D^*$ | $D_S/D_w$ | $\log n S_{Cs} n_A - \log n S_{Rb} n_A = D^*$ | $D_S/D_w$ |
|---|---|---|---|---|---|
| Sulfate | $H_2O$ | 0.26 | 1 | 0.06 | 1 |
| | $H_2O$ : $C_2H_5OH$=1 : 4 | 0.45 | 1.76 | 1.23 | 20.5 |
| Chloride | $H_2O$ | 0.16 | 1 | 0.10 | 1 |
| | HCl : $C_2H_5OH$=1 : 2 | 0.62 | 3.88 | 1.02 | 10.2 |
| | $H_2O$ : $C_2H_5OH$=1 : 25 | 0.45 | 2.81 | 0.80 | 8.0 |

$D^*$ : Dw means the D in water, $D_S$ means the D in solvent.

1) The value of $\log n S_{Rb} n_A / \log n S_K n_A$ changes with an increase of $n$ and becomes larger and larger with an increase of $R_{M.W.}$ except for $n=1$.

When $n=1$ $$\log S_{Rb}A / \log S_K A = \frac{1}{2}\left\{1-\left(\frac{R_{M.W.}}{500}\right)^2+\frac{R_{M.W.}}{200}\right\}$$

$n=2$ $$\log 2S_{Rb_2}A / \log 2S_{K_2}A = \frac{R_{M.W.}}{200}$$

$n=3$ $$\log 3S_{Rb_3}A / \log 3S_{K_3}A = \frac{3}{2}\left\{\left(\frac{R_{M.W.}}{500}\right)^2-1+\frac{R_{M.W.}}{200}\right\}$$

2) The value of $\log n S_{Rb} n_A - \log n S_{Cs} n_A$ is $n$ times as much as one at $n=1$ and becomes larger and larger with an increase of $R_{M.W.}$ and a decrease of W.

When $n=1$ $$\log S_{Rb}A - \log S_{Cs}A = \frac{1}{2}\left\{\frac{R_{M.W.}}{\left(1-\frac{R_{M.W.}}{1545}+\frac{W}{27}\right)\times 866}\right\}$$

$n=2$ $$\log 2S_{Rb_2}A - \log 2S_{Cs_2}A = \left\{\frac{R_{M.W.}}{\left(1-\frac{R_{M.W.}}{1545}+\frac{W}{27}\right)\times 866}\right\}$$

$n=3$ $$\log 3S_{Rb_3}A - \log 3S_{Cs_3}A = \frac{3}{2}\left\{\frac{R_{M.W.}}{\left(1-\frac{R_{M.W.}}{1545}+\frac{W}{27}\right)\times 866}\right\}$$

3) By lowering the dielectric constant of the solution, the solubility difference becomes much larger than that in an aqueous solution. Besides the solubility of these difficultly soluble salts, the deposition velocity of the precipitate has to be taken into account for the quantitative separation of potassium, rubidium and cesium. Situations where the differences in the deposition velocity are sufficient for the separation of these elements are found in the salts of heteropoly

acids such as silicotungstate,[1] silicomolybdate,[4] phosphomolybdate,[1][18] and phosphotungstate[18] *etc.* However the method using the difference in the deposition velocity seems to be inadequate for the quantitative separation of these elements because the solubility changes with time and therefore the specific separation is generally difficult.

Table 5. Chemical reactions with the various reagents.

| Compounds | Conditions | Solubility | | | Remarks |
|---|---|---|---|---|---|
| | | Potassium | Rubidium | Cesium | |
| $M_2 \cdot SnCl_6$[10] | Per 100ml of water, at 20°C | 0.1892 g | 0.0194 g | >D.S. | Separation is bad |
| $M_2 \cdot SnI_6$[19] | $K_2SnI_6$ reagent (aqueous solution) | V.S. | S. | F.S. | |
| $M_2 \cdot PbCl_6$ | $H_2PbCl$ in conc. HCl. | S. | F.S. | D.S. | Reagent is unstable |
| Phosphomolybdate | at 30°C | 0.204 g | > | > | Separation is not good |
| Silicomolybdate | 1000ml. of $H_2O$, at 20°C | F.S. | 4.1 g | 0.4 g | |
| Silicotungstate | 100grams of $H_2O$, at 20°C | F.S. | 0.69 g | 0.005 g | Separation is incomplete |
| $M_2NaBi(NO_2)_6$ | 3ml. of aq. soln. at 0°C | S. | Precipitate at more than 0.5 mg Rb | > | Solubility of R*is fairly large |
| $M_2AgBi(NO_2)_6$ | 4ml of aq. soln. at 0°C | S. | Precipitate at more than 0.02 mg Rb | > | Solubility of R*is small |
| $M_3 \cdot Bi_2I_9$ | 3ml. of conc. HAc at 0°C | S. | S. | Precipitate at more than 0.02mg Cs | Reaction is specific for cesium |
| $M_2AgCe(NO_2)_6$ | dil-HAc, at 0°C | S. | S. | F.S. | Cs-salt is yellow crystal |
| $M_2AuPdCl_7$[19] | Spot reaction | S. | F.S. | D.S. | |
| $M_2Au_2PtBr_{12}$[20] | Spot reaction | S. | F.S. | D.S. | |
| $M_3 \cdot Sb_2Cl_9$ | HCl or HAc | S. | F.S. | D.S. | |
| MCl-$SbCl_3$-$FeCl_3$ (triple salt) | HAc | S. | S. | F.S. | |

V.S. : very soluble. R* : Rb-salt
S. : soluble, no precipitate even in saturated solutions.
F.S. : fairly soluble, precipitate only in concentrated solutions.
D.S. : difficulty soluble.

## SEARCH FOR NEW REAGENT

From the above mentioned characteristics of the difficultly souble salts of potassium, rubidium and cesium, it is concluded that the most suitable reagent

for the quantitative separation of these elements has to fulfill the following conditions.

1) The number of alkali elements in the chemical formula of the precipitate produced by the reagent should be as large as possible.

2) $R_{M.W.}$ of the precipitate should be as large as possible.

3) The precipitate should have very little or preferably no water of crystallization.

4) The difficultly soluble salt should be capable of being produced in a suitable non-aqueous solvent.

Various reagents which were thought to satisfy most closely these conditions were experimentally studied and the results obtained as well as other known data are indicated in Table 5. According to Table 5, it is seen that the newly discovered $Na_2AgBi(NO_2)_6$ reagent is suitable for separating rubidium from potassium and that the $NaBiI_4$ or the $KBiI_4$ reagent is suitable for separating cesium from rubidium, when used in concentrated acetic acid rather than water.

As for the $Na_2AgBi(NO_2)_6$ reagent, the $R_{M.W.}$ is 593 and it is believed that the two sodium atoms in this reagent are replaced by rubidium or cesium atoms and therefore that $n$ is 2. Furthermore, the resulting precipitate is thought to be the following triple salt, $2MNO_2 \cdot AgNO_2 \cdot Bi(NO_2)_3$. Generally, in such a case, the solubility difference becomes much larger, and the value of the solubility difference between potassium and rubidium salts is large enough for the separation of potassium from rubidium as compared with those produced by the conventional reagents which have been used heretofore.

The chemical composition of the precipitate which is produced by the $NaBiI_4$ or the $KBiI_4$ reagent, as described later, is $Cs_3Bi_2I_9$ or $3CsI \cdot 2BiI_3$. So $R_{M.W.}$ is 1561 and $n$ is 3

Equation (2) does not hold for these values, because it has been derived from the data for aqueous solutions. However it is expected that the denominator the term $\frac{R_{M.W.}}{1545}$ in the equation (2) would give a much larger value in non-aqueous solutions and therefore that the value of $\log 3S_{Rb_3A} - \log 3S_{Cs_3A}$ would be a very large number.

## SUMMARY

The relationships of the solubility between the difficultly soluble salts of potassium and rubidium, rubidium and cesium have been quantitatively formulated from experimental data. From them, the necessary conditions for a maximum of solubility difference have been clarified. Reagents for the separation of these elements which would satisfy these conditions as much as possible were chosen and examined experimentally. As a result, it has been found that the $Na_2AgBi(NO_2)_6$ regent is suitable for separating rubidium from potassium and that the $NaBiI_4$ or $KBiI_4$ reagent in concentrated acetic acid is suitable for separating cesium from rubidium.

The former selectively reacts with rubidium and cesium and the latter with cesium. Therefore this study has established a foundation for future studies.

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